



PATENT SPECIFICATION

Application Date: June 3, 1937. No. 15469/37.

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PROVISIONAL SPECIFICATION

Process for the Manufacture of New Dyestuffs

I, ARTHUR CARPMAEL, British subject, of 24, Southampton Buildings, London, W.C.2, do hereby declare the nature of this invention (which has been communicated to me by I. G. Farbenindustrie Aktiengesellschaft, a joint stock company organised under the laws of Germany, of Frankfurt-on-Main, Germany), to be as follows:—

This invention relates to a process for the manufacture of new dyestuffs.

It has been found that valuable dyestuffs of the phthalocyanine series are obtained by heating phthalic acid-4-sulphonamides with copper salts in the presence of urea, suitably with the addition of compounds of elements of the fifth group such as molybdates, vanadates and phosphates or with the addition of boric acid. A modification of the said process consists in that 1,2-dihalogen-benzene-4-sulphonamides are heated with cuprous cyanide in the presence of quinoline. In both cases, i.e. in the case of using phthalic acid-4-sulphonamides as well as in the case of using 1,2-halogen-benzene-4-sulphonamides the hydrogen atoms of the sulphonamide group may be substituted by organic radicles.

The resulting phthalocyanines represent valuable dyestuffs showing bluish to greenish-blue shades and being characterised by excellent fastness properties. They are capable of being transformed into colour lakes, e.g. by causing them to react with alkaline earth metal salts, valuable pigment dyestuffs being thereby formed.

The phthalic acid sulphonamides serving as starting materials can be easily prepared by treating phthalic acid sulphochloride with ammonia or amines. The phthalic acid sulphonamides represent colourless well defined crystalline compounds which are mostly difficultly soluble in cold water but easily soluble in hot water.

The following examples illustrate the invention the parts being by weight:—

EXAMPLE 1.

39.1 parts of 1,2-dibromobenzene-4-sulphophenylamide are heated to boiling

with 180 parts of cuprous cyanide in 150 parts of quinoline for 5 hours. After cooling and adding caustic soda lye to the reaction mixture, the quinoline is blown off and the remaining bluish-green solution of the phthalocyanine tetraphenylsulphonamide is freed by filtration from copper. On the addition of acid the dyestuff is separated in the form of bluish flakes. After filtration with suction and drying it forms a blue-bronze mass which is easily soluble in aqueous alkalis.

EXAMPLE 2.

100 parts of phthalic acid-4-sulphonamide in 300 parts of urea are heated to 150° C. with the addition of 25 parts of cuprous chloride and 2 parts of ammonium molybdate whereupon the temperature is gradually raised to 180–190° C. When the formation of the dyestuff is complete, the melt is dissolved in hot dilute caustic soda lye, filtered from the copper still present therein, and the sodium salt is salted out by means of sodium chloride. On drying it forms a bronze-blue mass which is easily soluble in water, cotton being dyed therewith clear blue shades. On precipitating the dyestuff by means of barium chloride there is obtained a brilliant lake dyestuff suitable for graphic prints.

EXAMPLE 3.

To a mixture of 100 parts of phthalic acid-4-phenyl sulphonamide (colourless leaflets of M.P. 193–194° C. with foaming) and 300 parts of urea there are added at 150° C. 25 parts of copper chloride, 2 parts of boric acid and 2 parts of ammonium molybdate, whereupon the reaction mixture is heated to 180–190° C. and kept at this temperature until the formation of the dyestuff is complete. Thereupon the melt is dissolved in hot dilute caustic soda lye, freed from excess copper and acidified, the dyestuff thus precipitating in the form of bluish-green flakes. On drying it forms a bronze-blue mass which is easily soluble in dilute caustic soda lye with a bluish-green coloration. It is also easily soluble in pyridine and other organic solvents.

EXAMPLE 4.

100 parts of phthalic acid-4-methyl
phenyl sulphonamide (which is obtained
by condensing phthalic acid sulpho-
chloride with monomethylaniline) and
300 parts of urea are heated to 150° C.
To this melt there are added 25 parts of
cuprous chloride, 2 parts of boric acid
and 2 parts of ammonium molybdate,
10 heating being continued to 200–210° C.
until the formation of the dyestuff is
complete. Thereupon the melt is boiled

with dilute hydrochloric acid, filtered
with suction, washed neutral and dried.
The dyestuff thus obtained forms a bluish- 15
green powder which is insoluble in
alkalies.

Dated this third day of June, 1937.

CARPMAELS & RANSFORD,
Agents for Applicant,
24, Southampton Buildings,
London, W.C.2.

COMPLETE SPECIFICATION

Process for the Manufacture of New Dyestuffs

I, ARTHUR CARPMAEL, British subject,
of 24, Southampton Buildings, London,
W.C.2, do hereby declare the nature of
this invention (which has been communi-
cated to me by I. G. Farbenindustrie
Aktiengesellschaft, a joint stock company
organised under the laws of Germany, of
Frankfort-on-Main, Germany), and in
what manner the same is to be performed,
to be particularly described and ascer-
tained in and by the following state-
ment:—

This invention relates to a process for
the manufacture of new dyestuffs.

Specification No. 464,126 describes and
claims inter alia a process for the manu-
facture of stable metal phthalocyanines
which comprises heating together a
phthalic acid with a urea and a copper
salt and Specification No. 464,673 which
is for a patent of addition thereto
describes and claims effecting the reac-
tion in the presence of a small quantity
of boric acid. Specification No. 476,243,
which was not published at the date of
the present application, claims an
improvement in the process claimed in
Specification No. 464,126, if desired as
modified as described in Specification No.
464,673, which comprises carrying out the
said process in the presence of an ancillary
agent being a substance consisting of or
containing an element of group V or VI
of the Periodic System according to
Mendeleef and having an Atomic Number
between 15 and 23 or between 33 and 92
each inclusive.

It has been found that valuable dye-
stuffs of the phthalocyanine series are
obtained by heating phthalic acid-4-
sulphonamides with copper salts in the
presence of urea, suitably with the addi-
tion of compounds of elements of the fifth
group such as molybdates, vanadates and
phosphates or with the addition of boric
acid. A modification of the said process
consists in that 1,2-dihalogen-benzene-4-
sulphonamides are heated with cuprous

cyanide in the presence of tertiary
amines such as quinoline. In
both cases, i.e. in the case of using
phthalic acid-4-sulphonamides as well as
in the case of using 1,2-halogen-benzene-
4-sulphonamides the hydrogen atoms of
the sulphonamide group may be substi-
tuted by organic radicles.

The resulting phthalocyanines repre-
sent valuable dyestuffs showing bluish to
greenish-blue shades and being charac-
terised by excellent fastness properties.

The products of the present invention
have the advantage over those described
in the specifications referred to above
that they are more stable in the vatted
state. In so far as they still contain
hydrogen atoms attached to the nitrogen
of the sulphonamide group they are
capable of being transformed into colour
lakes, e.g. by causing them to react with
alkaline earth metal salts, valuable pig-
ment dyestuffs being thereby formed.
Moreover, depending on the nature of the
substituents which may be present in the
sulphonamide group, the products may
be soluble in various organic solvents (cf.
Examples 5 and 6).

The phthalic acid sulphonamides serv-
ing as starting materials can be easily
prepared by treating phthalic acid
sulphochloride with ammonia or amines.
The phthalic acid sulphonamides repre-
sent colourless well defined crystalline
compounds which are mostly difficultly
soluble in cold water but easily soluble
in hot water.

The following examples illustrate the
invention the parts being by weight:—

EXAMPLE 1.

39.1 parts of 1,2-dibromobenzene-4-
sulphophenylamide are heated to boiling
with 180 parts of cuprous cyanide in 150
parts of quinoline for 5 hours. After
cooling and adding caustic soda lye to the
reaction mixture, the quinoline is blown
off and the remaining bluish-green solu-

tion of the phthalocyanine tetraphenylsulphonamide is freed by filtration from copper. On the addition of acid the dyestuff is separated in the form of bluish flakes. After filtration with suction and drying it forms a blue-bronze mass which is easily soluble in aqueous alkalis.

EXAMPLE 2.

100 parts of phthalic acid-4-sulphonamide in 300 parts of urea are heated to 150° C. with the addition of 25 parts of cuprous chloride 2 parts of boric acid and 2 parts of ammonium molybdate whereupon the temperature is gradually raised to 180—190° C. When the formation of the dyestuff is complete, the melt is dissolved in hot dilute caustic soda lye, filtered from the copper still present therein, and the sodium salt is salted out by means of sodium chloride. On drying it forms a bronze-blue mass which is easily soluble in water. On precipitating the dyestuff by means of barium chloride there is obtained a brilliant lake dyestuff suitable for graphic prints.

EXAMPLE 3.

To a mixture of 100 parts of phthalic acid-4-phenyl sulphonamide (colourless leaflets of M.P. 193—194° C. with foaming) and 300 parts of urea there are added at 150° C. 25 parts of copper chloride, 2 parts of boric acid and 2 parts of ammonium molybdate, whereupon the reaction mixture is heated to 180—190° C. and kept at this temperature until the formation of the dyestuff is complete. Thereupon the melt is dissolved in hot dilute caustic soda lye, freed from excess copper and acidified, the dyestuff thus precipitating in the form of bluish-green flakes. On drying it forms a bronze-blue mass which is easily soluble in dilute caustic soda lye with a bluish-green colouration. It is also easily soluble in pyridine and other organic solvents.

EXAMPLE 4.

100 parts of phthalic acid-4-methyl phenyl sulphonamide (which is obtained by condensing phthalic acid sulphonyl chloride with monomethylaniline) and 300 parts of urea are heated to 150° C. To this melt there are added 25 parts of cuprous chloride, 2 parts of boric acid and 2 parts of ammonium molybdate, heating being continued to 200—210° C. until the formation of the dyestuff is complete. Thereupon the melt is boiled with dilute hydrochloric acid, filtered with suction, washed neutral and dried. The dyestuff thus obtained forms a bluish-green powder which is insoluble in alkalis.

EXAMPLE 5.

An intimate mixture of 10 parts of phthalic acid-4-*n*-butylsulphonamide, 30 parts of urea, 2 parts of copper chloride and 0.1 part of ammonium molybdate is heated to 180° C. until the formation of the dyestuff is complete. Thereupon the melt is diluted with dilute hydrochloric acid, heated to boiling and filtered with suction. The dyestuff thus obtained is a greenish-blue powder which is soluble in dilute caustic soda lye, pyridine, dioxane and acetone. It is probably a phthalocyanine tetra-*n*-butylsulphonamide.

EXAMPLE 6.

An intimate mixture of 10 parts of phthalic acid-4-isobutylsulphonamide, 30 parts of urea, 2 parts of copper chloride and 0.1 part of ammonium molybdate is melted at about 180° C. until the formation of the phthalocyanine is complete. Thereupon the melt is boiled with dilute hydrochloric acid, filtered with suction and dried. The dyestuff thus obtained is a greenish-blue powder which is soluble in dilute caustic soda lye, pyridine, dioxane and acetone.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. The manufacture of dyestuffs by heating copper salts with phthalic acid-4-sulphonamides in the presence of urea, if desired with the addition of compounds of elements of the fifth group such as molybdates, vanadates and phosphates or with the addition of boric acid.

2. A modification of the process claimed in claim 1 wherein 1,2-dihalo-benzene-4-sulphonamides are heated with cuprous cyanide in the presence of tertiary amines.

3. The manufacture of dyestuffs substantially as described in the examples.

4. Process as claimed in any of claims 1—3, wherein the resulting phthalocyanine sulphonamides in so far as they still contain a hydrogen atom attached to the nitrogen are subsequently converted into their alkaline earth metal salts.

5. Phthalocyanine sulphonamides whenever prepared or produced by a process claimed in any of the preceding claims or by any process which is an obvious chemical equivalent thereof.

Dated this 3rd day of June, 1938.

CARPMAELS & RANSFORD,
Agents for Applicant,
24, Southampton Buildings,
London, W.C.2.